

# HAZARD ANALYSIS FOR THE PROTECTION OF PV MANUFACTURING FACILITIES

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## ABSTRACT

Photovoltaic manufacturing facilities use toxic, corrosive or flammable substances, which, if not handled properly can present environmental, health and safety (EHS) risks. Although the amounts of hazardous substances used in the PV industry are far smaller than those used in the chemical industry, such substances can present EHS hazards. As PV manufacturing is scaled-up to meet a growing demand, preserving the safe and friendly to the environment nature of PV becomes even more important. This paper presents a systematic approach and specific methods of accident prevention that are available to the industry. As the PV industry approaches accident prevention in a systematic and vigilant way, the risk to the industry and the public will be minimized.

## 1. MULTI-LAYER PROTECTION

A comprehensive approach for accident prevention and minimization of EHS risks, includes several layers of protection. Administrative & engineering options to prevent and control accidental releases and reduce their consequences are considered sequentially in six steps; each one adding a layer of protection [1].

- (i) Inherently safer technologies, processes and materials.
- (ii) Safer use of material (e.g. safer forms of a chemical, reduced on-site inventories, high material utilization and on-demand generation).
- (iii) Options to prevent accident-initiating events (e.g. safer designs, process hazard analysis (PHA), operating and maintenance procedures and detection and monitoring systems).
- (iv) Safety systems to prevent or minimize releases at the source (e.g. automatic shut-offs, flow-restricting valves and cooling and containment systems).
- (v) Systems to capture accidental releases (e.g. secondary confinement, emergency-handling scrubbers and incinerators and adsorbers).
- (vi) Options to prevent or minimize human exposures and their consequences (e.g. separation zones, physical barriers, emergency preparedness and response plans and evacuation plans).

### 1.1. Selection of Technology, Process and Materials

The most efficient strategy to reduce hazards is to choose technologies and processes that do not require the use of large quantities of hazardous gases. This is especially important for new technologies, where this approach can be implemented early in development before large financial

resources and efforts are committed to specific options. Life-cycle considerations are necessary in evaluating technology options and associated safety and environmental control costs, because some technologies present mainly occupational risks (e.g. a-Si) while others present mainly end-of-life concerns (e.g. CdTe).

### 1.2 Safer Use of Materials

This strategy can be implemented as: substitution (i.e. using safer material or environmentally more benign ones), use of a safer, less mobile form of a hazardous material; point-of-use generation; and reduction of the quantity or concentration of a hazardous material in process and storage. Alternatives need careful evaluation because there are frequently both advantages and disadvantages associated with every option.

#### Substitution

As example of substitution consider tertiary-butylarsine (TBA) and tertiary-butylphosphine (TBP) in place of arsine and phosphine, in the MOCVD of GaAs-based cells. These metal-organic compounds combine a safer physical form (i.e. liquid versus gas) and lower toxicity (although potential for carcinogenicity exists) than the corresponding inorganic hydrides. Both compounds are strong reducing agents and may ignite if they are dispersed and exposed to oxidizers, but they are not explosively pyrophoric. It appears that there are no technical barriers for these replacements [2].

Another example is solid selenium as an alternative to hydrogen selenide for CIS and CIGS cells. Solid sources eliminate the risks associated with accidental release from storage, but not from processing. Solid sources are vaporized at 700-900 °C and the vapors are transported into the deposition chambers; the potential therefore exists for accidental vapor releases from the vaporizers. The technical disadvantages of solid sources are the increased set-up time and maintenance, both of which can raise the manufacturing costs.

#### Safer forms

Sub-atmospheric pressure sources have developed as safer delivery sources (SDS™) of dopant gases (e.g. arsine, phosphine, boron trifluoride, germane and silicon tetrafluoride) [3]. The SDS comprises adsorbent media in a standard compressed-gas cylinder, which reversibly adsorbs the dopant gas. The cylinder is charged with the dopant gas to a pressure slightly less than one atmosphere and uses pressure-swing (vacuum) desorption to deliver the dopant to

the low-pressure process. This technique effectively changes the source from a high-pressure gas to essentially a solid and greatly reduces the risks related to leakage of these materials; it reduces both the probability of a leak and the associated consequences. Independent tests show that the worst-scenario releases of arsine, phosphine and boron trifluoride from SDS would cause concentrations below half of the corresponding Immediately Dangerous to Life or Health (IDLH) levels and, therefore, SDS eliminates the need for isolating the process and for catastrophic-release scrubbers.

Higher material utilization rate.

Some processes have much higher rates of material use than others (e.g. hot-wire deposition vs. plasma -discharge deposition of silane, in a-Si deposition; electrodeposition vs. spray pyrolysis in CdTe and CdS deposition). For hazardous chemicals, higher utilization rates offer safety advantages in addition to lower costs; the lower the amounts of chemicals used and stored in a facility, the lower the related potential risks. As PV reaches higher levels of commercialization, processes with low efficiency will have to be improved or unused materials will have to be captured, purified and reused.

### 1.3. Prevention of Initiating Events

Once specific materials and systems have been selected, strategies to prevent accident-initiating events need to be evaluated and implemented. In the USA, facilities that handle highly hazardous chemicals above certain threshold quantities are required to comply with the Occupational Safety and Health Administration (OSHA) Process Safety Management (PSM) Rule and the Environmental Protection Agency (EPA) Risk Management Program (RMP). The OSHA PSM focuses on accident prevention, whereas the EPA RMP expands beyond prevention to the mitigation of the consequences of an accident. About 180 materials are presently listed in these rules; some of these materials are used in PV manufacturing. Most of today's PV facilities are not subject to compliance with these rules because they quantities smaller than the threshold quantities. Nevertheless, a pro-active approach for minimizing risks is to the utmost advantage of the PV industry and, the OSHA and EPA provisions should taken as guidance for all PV facilities that handle highly hazardous materials. Perhaps the most important item in a PSM is the process-hazard analysis (PHA). Hazard analyses focus on equipment, instrumentation, utilities, human actions and external factors that might impact the process and cause an accident-initiating event.

## 2. PROCESS HAZARD ANALYSIS FOR THE PROTECTION OF PV FACILITIES

The purpose of process hazard analysis (PHA) is to determine if credible accident initiating events exist. PHA should consider planned and unplanned actions and events, related to both systems and human interactions. All hazard analyses are team activities. The team should include individuals that understand well the system and a facilitator

who is organized and can draw the participation and contributions of the employees. The team composition is as important as the technique itself. PHA methods range from the simple Checklist or What if analyses that require only a few hours of meetings to the very comprehensive FTA that requires 1-3 months of effort.

## 3. "WHAT IF" ANALYSIS

The "What if" analysis is a brainstorming approach in which a team of individuals knowledgeable with a process ask questions in the form of "What if" related to equipment or other system failures, and procedural errors. For example: "What if power to the exhaust blower X is lost?", or "what if relief valve Y fails to open?" Through the questioning process, an experienced team of individuals can identify accident situations and their consequences, evaluate existing safeguards and suggest risk reductions measures.

The degree of thoroughness in the application of this method is largely dependent upon the team composition. The team must include at least one person with good knowledge of the process. For simple systems, at total of 2 or 3 people with interdisciplinary background may be assigned to perform the analysis. The team must be well organized to ensure that the "what if" questions were exhausted. This is a simple method, which can produce results in a few hours of meetings. It is useful for relatively simple systems, but may not help in identifying the potential for multiple failures or synergistic effects [4].

A more systematic method is HAZOP.

## 4. HAZARD AND OPERABILITY ANALYSIS (HAZOP)

HAZOP is a structured analysis of a system, process unit or operation, with the goal to identify accident-initiating scenarios. The HAZOP team conducts a stage-by-stage examination of a design and intent of a system or operation. The system to be studied is divided to sections (nodes) that provide a logical breakdown of major subsystems for examination. For example, a typical chemical vapor deposition (CVD) process may be divided to the following nodes: gas panel, liquid delivery system, process reactor, vacuum pump, and pollution control system. Once the nodes are selected, the analyst should obtain all documentation documents, including drawings (PIDs and PFDs), component specifications, and logical control programs. The analysis aims in being systematic and rigorous yet open and creative. HAZOP utilizes a set of guidewords (e.g., none, more, high), in combination with the system parameters to seek physically possible deviations from the design intent (e.g., no flow, high pressure or high temperature). The team concentrates on those deviations that could lead to potential EHS risks. When causes of a deviation are found, the team screens the potential consequences based on their experience; for consequences with undesirable potential,

consequence analysis tools (e.g., atmospheric dispersion models, blast analysis models) are used to quantify the level of consequences.

A prerequisite for a HAZOP study is a well developed design. If the drawings are incomplete or inaccurate, the study would be worthless. The boundaries (nodes) of the study must be clearly analyzed and studied. A clear description and design intention must be given to every section of the design, which is analyzed. As with all PHA methods, the study team must combine knowledge and experience [4,5].

An even more comprehensive process hazard analysis is Fault Tree Analysis (FTA).

## 5. FAULT TREE ANALYSIS

Fault tree analysis can be used to determine failure sequences and failure probabilities of complex and undesirable events, “*such as major fire and failure of automatic fire protection system,*” and to understand their possible causes in terms of more basic events, “*such as loss of electrical power to firewater system,*” and even more basic events, such as “*power cable damaged in fire.*”

A fault tree is a picture of the logical relationships between the primary events (e.g., failures of specific components), the intermediate events (e.g., failure of one part of a safety system as a function of failures of various components), and the top event (e.g., failure of containment and release to the environment). To construct a fault tree, the failure of interest is designated as a top event. Tracing backwards, all failures that could lead to the top event are identified. This process continues until failures are reached that cannot be reduced any more, or cannot be quantified.

This set of logical relationships can be processed using Boolean algebra to provide a logical expression relating the top event to combinations of primary events. In one form of this expression, each term is a combination of primary events that is a **minimal cut set**: *a combination that is sufficient to cause the top event.* Given the likelihood of the primary events, this expression can serve as a basis for quantifying the likelihood of the top event, and it contains a great deal of information about the causes of the top event. FTA is useful in particular contexts, which are characterized below:

### Hypothetical Consequences of an Accident are Unacceptable

If a facility handles a large quantity of hazardous substances, and the potential consequences of an accident are extremely undesirable, then a comprehensive hazard analysis is warranted. The systematic nature of FTA is particularly valuable in this context, and the relatively high level of effort associated with FTA can be justified.

### Safety Case for a Facility Depend on Multiple Layers of Defense (Safety Systems, Fire Extinguishing Systems, Plant Trip Logic, etc.)

Multiple layers of defense exist at some facilities handling potentially hazardous materials, such that a release requires failure or bypass of these layers of defense. The reason for having multiple layers is that if they are independent, failure of all of them can be made extremely unlikely. Under rather simple assumptions, it can be argued that two layers failing with probabilities of  $10^{-3}$  each is an easier design to realize than one layer at  $10^{-6}$ , because  $10^{-6}$  is an extremely small failure probability that cannot be easily supported in light of phenomenological uncertainty, common cause, etc. Therefore, a common strategy is to go for multiple layers of defense, each reasonably unlikely to fail, in the hope that failure of the combination is essentially incredible. This hope is only realized if the layers are completely independent. Much of the reason for undertaking fault tree analysis boils down to the need to look for circumstances that compromise the hypothetical independence of redundant layers of defense. In particular, it is necessary to be on the lookout for conditions that adversely affect a given layer of defense at the same time that they produce a safety challenge to that layer (e.g., a fire that takes out a fire suppression system or a loss of electrical power that simultaneously creates a plan transient and deprives a mitigating system of power).

### Complex Systems

The failure modes associated with all but the simplest systems are too complex to study without the aid of computers. Fault trees are a simple and unambiguous way to organize a comprehensive logic model for computer analysis.

## 6. CONCLUSION

It is of the utmost importance for the future of the PV industry to prevent/ minimize accidental releases of hazardous gases by selecting safer technologies, processes, and materials, using materials more efficiently and in safer forms, and emphasizing employee training and safety procedures. For facilities that use hazardous materials in forms and quantities that can cause harm, Process Hazard Analysis (PHA) is recommended to identify all potential accident initiating events so that they can be prevented or mitigated. PHA methods range from the simple Checklist or What if analyses that require only a few hours of meetings to the very comprehensive FMEA or FTA that require 1-3 months of effort. The later are justified for complex systems or when potential consequences are unacceptable. A compilation of PHA examples specific to photovoltaic manufacturing is in progress.

PHA can identify design or system modifications, which increase safety in a facility. As the PV industry approaches accident prevention in a systematic way, the risk to the industry and the public will be minimized.

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